Applications of anodized TiO$_2$ films for environmental purifications

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Abstract

The high performance photocatalytic TiO$_2$ films were successfully obtained by a galvanostatic anodization of metallic titanium using the optimum anodization condition, subsequent to pre-nitridation treatment. The optimized anodization parameters on the formation of high photocatalytic TiO$_2$ film were investigated. The pre-nitridation treatment was performed by annealing metallic Ti under a nitrogen atmosphere of 0.1 MPa. The anodized TiO$_2$ film showed the high photocatalytic activities to decompose not only gaseous acetaldehyde but also tetrachloroethylene, which revealed that the anodized TiO$_2$ film is a possible candidate of the photocatalyst for environmental purifications comparable to the best photocatalyst of fine crystalline powder.
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Keywords: TiO$_2$; Anodization; Pre-nitridation; Photocatalytic activity; Tetracholoroethylene

1. Introduction

TiO$_2$ photocatalysts are attractive and promising materials due to their excellent properties such as a high photocatalytic activity, stability, and non-toxicity. Especially, the high photocatalytic activity of TiO$_2$ has received much attention; therefore it has applied into various fields such as a purification of air and water [1–4], splitting of water into hydrogen [5,6], bactericidal action [7–9], and dye-sensitized solar cells [10,11].

The major forms of TiO$_2$ photocatalysts are nano-sized fine particles in order to obtain high surface areas [12,13]. The coating procedures of the fine TiO$_2$ particles on the substrate must be used binder chemicals in order to fabricate commercial applications [14–16]. However, the fine TiO$_2$ particles slightly scatter at the surface of a specimen, since most particles are buried in binder chemicals, leading to obtaining a low photocatalytic activity.

On the other hand, TiO$_2$ films can be easily formed on a Ti metal substrate by anodization using various electrolytes. However, the amorphous TiO$_2$ films with no photocatalytic activities are usually obtained in a conventional anodization using a H$_3$PO$_4$ as an electrolyte. Some researchers have investigated fabrications of the high performance photocatalytic TiO$_2$ films by anodization. For instance, Kuraki et al. [17] prepared TiO$_2$ films by anodization at an applied voltage of 150–200 V in an acidic electrolyte composed of 1.5 M H$_2$SO$_4$, 0.3 M H$_3$PO$_4$, and 0.3 M H$_2$O$_2$, but the obtained films hardly showed any photocatalytic activity due to an existence of a low valence oxide phase such as TiO and Ti$_2$O$_3$, which retarded the photocatalytic activity. The photocatalytic anodized TiO$_2$ films could be fabricated by re-anodization in a mixture of NH$_4$HF$_2$ and H$_2$O$_2$, which effectively removed the low valence oxide phase created as a byproduct in the anodization process. Kuraki et al. [17] reported that the anodized TiO$_2$ films with the low valence oxide have gray color, while those without the low valence oxide have white color. Therefore, the existence of low valence oxide which retards photocatalytic activity can monitor by measuring L value (lightness) in surface of anodized specimens. TiO$_2$ nanotube arrays were fabricated by anodization using an electrolyte containing HF [18,19]. However, the as-anodized TiO$_2$ nanotubes were amorphous, post-annealing treatments were performed in order to obtain the high performance TiO$_2$. The authors have developed a new fabrication method for obtaining the high photocatalytic TiO$_2$ films by using a combined treatment of pre-nitridation and potentiostatic anodization in an acidic electrolyte composed of 1.5 M H$_2$SO$_4$, 0.3 M H$_3$PO$_4$, and 0.3 M H$_2$O$_2$ [20].

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Several volatile organic chlorinated compounds such as a tetrachloroethylene (perchloroethylene, PCE) are used as solvents in dry cleaning and metal degreasing facilities [21–23]. PCE is toxic, carcinogenic, and extremely persistent in the environments. Therefore, the effective degrading technologies of PCE have received much attention. The TiO_2 photocatalysts are possible candidates for the photodegradation of PCE.

In this study, the photocatalytic degradation of a tetrachloroethylene using the anodized TiO_2 films with a pre-nitridation treatment was investigated. To obtain the high performance photocatalytic anodized TiO_2 films, the effect of anodization parameters such as anodization times, current densities, temperatures of electrolyte, and electrolyte compositions on the photocatalytic activity for decomposition of acetaldehyde were also investigated.

2. Experimental

A Ti plate with purity of greater than 99.5% (Nippon Steel Corporation) was electrolytically degreased and etched in 5% HF aqueous solution for 2 min at room temperature. The Ti plate was annealed under a nitrogen atmosphere of 0.1 MPa for 6 h with a furnace (GR-6156-15-S, Koyo Thermo System Co. Ltd.). The degree of formation of TiN films by the annealing treatment was evaluated by monitoring the X-ray diffraction (XRD) integrated intensity. The XRD measurement was conducted by using an X-ray diffractometer (M18X-CE, Bruker AXS, Cu Kα radiation, operated at 40 kV and 100 mA). It is well-known that a surface hardness of the specimens can be improved by coating TiN film on the specimens. A surface hardness of nitrided specimens was measured with the Vickers hardness. The formed TiN film by the annealing was also characterized by using X-ray photo-electron spectroscopy (XPS) analysis with a Quantum-2000 (ULBAC-PHI Inc., Japan, Al Kα radiation).

The nitrided titanium plate was galvanostatically anodized using a DC power supply (PU-300-5, Kenwood Corporation). A temperature of electrolyte was controlled by using water bath equipped with a chiller. The obtained anodized TiO_2 films were also analyzed with the XRD. The degree of anatase TiO_2 film formation was evaluated by monitoring the XRD integrated intensity of 1 0 1 reflection in which 2θ is 25.4°. For investigation of the existence of low valence oxide which retarded photocatalytic activity, the L value of the obtained anodized TiO_2 films was measured with colorimeter (CR-100, Minolta). The morphologies of anodized a films were observed using a scanning electron microscope (S-2380, Hitachi High-Technologies Corporation). The surface areas of the obtained anodized TiO_2 films were also evaluated by measuring the amount of chemisorbed dye on the TiO_2 surface. It is well-known that N 719 dye (Solaronix) can adsorb on the surface of TiO_2. The amount of adsorbing dye on the anodized TiO_2 films is considered to be closely related to the surface area of TiO_2. The anodized TiO_2 specimens were immersed into the dye solution composed of 0.3 mM of N 719 in t-butanol/acetonitrile (1:1 in volume fraction) at 40 °C for 3 days. Afterwards, the amount of adsorbed dye on the anodized TiO_2 films was

determined by the measurement of the concentration of the dye desorbed from the surface of the anodized TiO_2 films into a mixed solution of 0.1 M NaOH and ethanol (1:1 in volume fraction) with a UV-mini 1240 (Shimadzu). Since the desorbed dye solution has absorption maximum of 308 nm, the surface area of the anodized TiO_2 films was determined by monitoring the absorbance of the desorbed dye solution at a wavelength of 308 nm.

Photodecomposition of acetaldehyde is usually utilized for an evaluation of photocatalytic activity [24–27]. For obtaining the optimum anodization parameters, the photocatalytic activities of the anodized TiO_2 films were determined by monitoring decomposition of gaseous acetaldehyde. The reaction container (Tedlar® bag) containing 3 dm^3 of 100 ppm of gaseous acetaldehyde and the anodized sample (surface area = 100 cm^2) was irradiated from a top side. The gaseous acetaldehyde was prepared by diluting regent of acetaldehyde (Wako Chemicals, purity greater than 90%) with air. A fluorescent lamp emitting in the near-UV region was used in this study. An excitation light intensity of approximately 2 mW/cm^2 was obtained at the surface of the specimens. The concentration of gaseous acetaldehyde was monitored using Gastec standard detector tube system (gas sampling pump GV-100, acetaldehyde detection tube No. 92M or 92L) [28].

The photocatalytic activities of the anodized TiO_2 films were also evaluated by monitoring decomposition of gaseous tetrachloroethylene. The reaction container (Tedlar® bag) containing 3 dm^3 of 40 ppm of gaseous tetrachloroethylene and the anodized sample (surface area = 100 cm^2) was also irradiated from a top side. The gaseous tetrachloroethylene was prepared by diluting regent of tetrachloroethylene (Wako Chemicals, purity greater than 99.0%) with air. The evaluation of decomposition of gaseous tetrachloroethylene was performed using the same system of that of acetaldehyde. The concentration of gaseous tetrachloroethylene was also monitored using Gastec standard detector tube system (gas sampling pump GV-100, tetrachloroethylene detection tube No. 133M or 133L) [21].

3. Results and discussion

Fig. 1 shows the integrated XRD intensity of formed TiN phase of 1 1 1 reflection as a function of annealing temperature. It is clearly seen that the TiN integrated XRD intensity apparently increased with increasing annealing temperature. It is well-known that a surface hardness of the specimens can be improved by coating a TiN film on the specimens [29–31]. Chou et al. [29] reported that the hardness of TiN films increased with increasing the formation of TiN (1 1 1) phase. Fig. 2 shows the Vickers hardness of nitrided specimens as a function of annealing temperature. The degree of increasing the integrated XRD intensity was strongly dependent on the increasing the Vickers hardness of the nitrided specimens. Fig. 3 shows the N 1s line of XPS spectrum of the nitrided specimens. The chemical state of nitride compound is usually characterized by the binding energy of the N 1s line [32]. From the result in Fig. 3, the N 1s peak is found at approximately
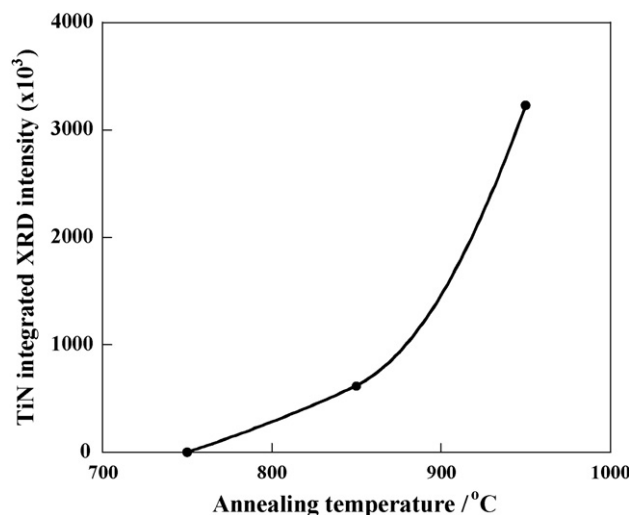
Fig. 1. Integrated XRD intensity of formed TiN phase of 1 1 1 reflection as a function of annealing temperature. Ti plate was annealed for 6 h under a nitrogen atmosphere at 0.1 MPa.

Fig. 3. N 1s line of XPS spectrum of the nitrided specimens. Ti plate was annealed at 950 °C under a nitrogen atmosphere at 0.1 MPa.
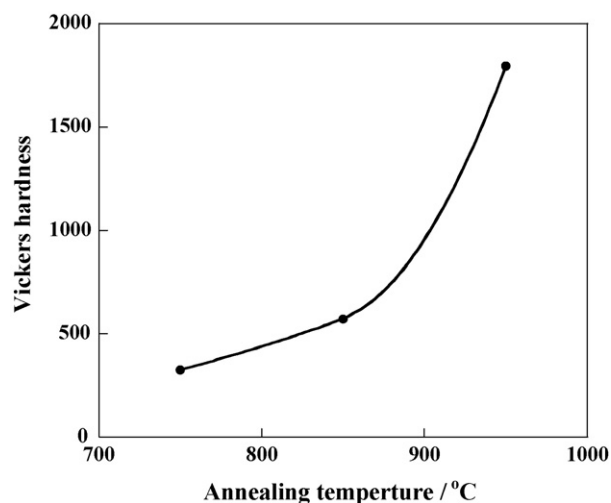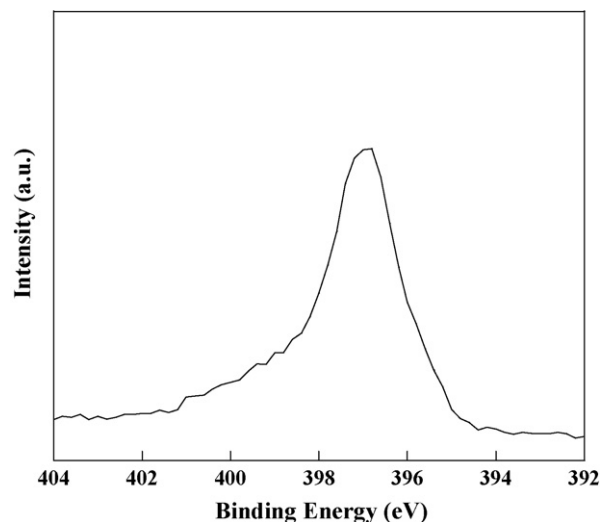

Fig. 2. Vickers hardness of nitrided specimens as a function of annealing temperature. Ti plate was annealed for 6 h under a nitrogen atmosphere at 0.1 MPa.
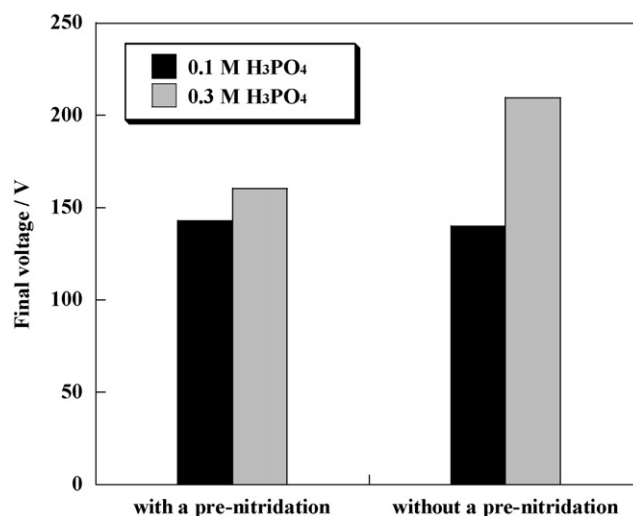

Fig. 4. Final voltages during anodization with and without pre-nitridation. Anodization was conducted by using electrolyte composed of 1.5 M H_2SO_4 and 0.3 M H_2O_2 with varying H_3PO_4 concentrations into 0.1 and 0.3 M, respectively.

396.7 eV of binding energy. Bertóti [32] reported that N 1s peak in TiN was found at 397.6 eV of binding energy. Therefore, TiN formation can be confirmed by the XPS spectrum. From these characterizations, TiN film can be formed on metallic titanium by simple heating treatment of Ti under a nitrogen atmosphere of 0.1 MPa.

For investigation of the effect of pre-nitridation on the formation of photocatalytic anodized anatase TiO_2 films, Ti plates with and without pre-nitridation were anodized for 30 min using electrolyte composed of 1.5 M H_2SO_4 and 0.3 M H_2O_2 with varying H_3PO_4 concentrations into 0.1 and 0.3 M, respectively. A temperature of electrolyte and a current density was set at 20 °C and 1.0 A/dm^2, respectively. Fig. 4 shows the final voltages during anodization with and without pre-nitridation. The final voltage during anodization with pre-nitridation is lower than that without pre-nitridation when using electrolyte composed of 1.5 M H_2SO_4, 0.3 M H_3PO_4, and

0.3 M H_2O_2. The final voltage during anodization using electrolyte containing 0.1 M H_3PO_4 showed lower value than that using electrolyte containing 0.3 M H_3PO_4.

Fig. 5 shows the formation of anatase TiO_2 films during anodization by monitoring the integrated XRD intensity of 1 0 1 reflection. The anodized TiO_2 film with pre-nitridation has higher formation of anatase TiO_2 than that without pre-nitridation when using electrolyte composed of 1.5 M H_2SO_4, 0.3 M H_3PO_4, and 0.3 M H_2O_2. The formations of anatase TiO_2 during anodization using electrolyte containing 0.1 M H_3PO_4 are almost same between anodized specimens with and without pre-nitridation. The degree of formation of anatase TiO_2 film is strongly dependent on the final voltage during anodization, as shown in Figs. 4 and 5.

Fig. 6 shows L value of anodized specimens with and without pre-nitridation. It is clearly seen that L values of anodized specimen with pre-nitridation are higher than those
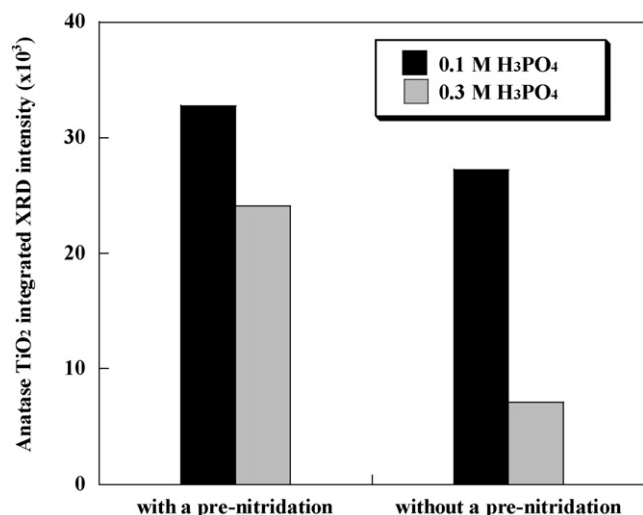
Fig. 5. Formation of anatase TiO_2 films during anodization with and without pre-nitridation by monitoring the integrated XRD intensity of 1 0 1 reflection. Anodization was conducted by using electrolyte composed of 1.5 M H_2SO_4 and 0.3 M H_2O_2 with varying H_3PO_4 concentrations into 0.1 and 0.3 M, respectively.
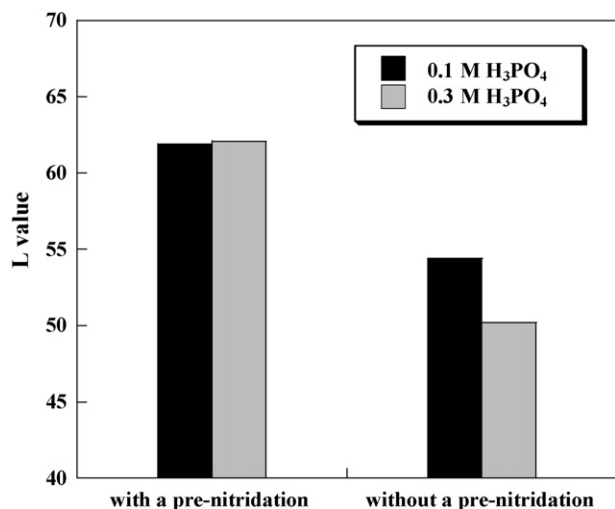

Fig. 6. L (lightness) value of anodized specimens with and without pre-nitridation. Anodization was conducted by using electrolyte composed of 1.5 M H_2SO_4 and 0.3 M H_2O_2 with varying H_3PO_4 concentrations into 0.1 and 0.3 M, respectively.

without pre-nitridation. In Fig. 6, the anodized specimens with pre-nitridation have smaller amount of low valence oxide which retarded photocatalytic activities, compared with those without pre-nitridation.

Fig. 7 shows the photocatalytic decomposition of acetaldehyde by anodized TiO_2 films with and without pre-nitridation. Ti plates with and without a pre-nitridation were anodized for 30 min using an electrolyte composed of 1.5 M H_2SO_4, 0.1 M H_3PO_4, and 0.3 M H_2O_2. A temperature of electrolyte and a current density was set at 20 °C and 1.0 A/dm^2, respectively. It is clearly seen that a pre-nitridation treatment has an accelerating effect on the photocatalytic activities of the anodized TiO_2 films for a photodegradation of acetaldehyde. The passive TiO_2 film formed on Ti metal acts as a barrier to prevent further anodization
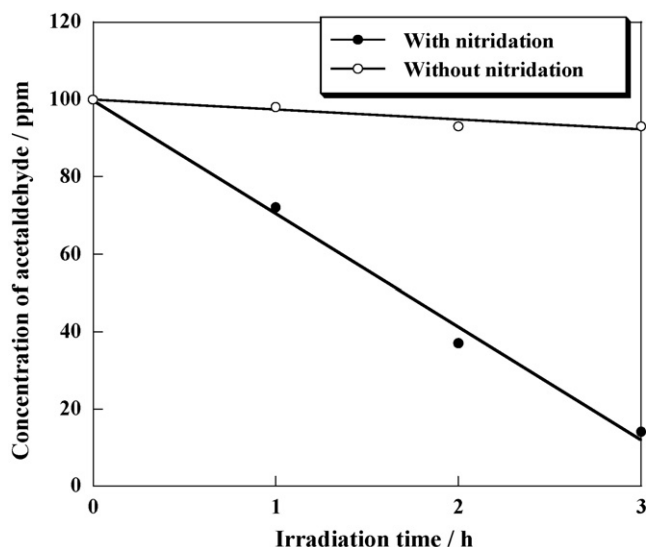

Fig. 7. Photocatalytic decomposition of acetaldehyde by anodized TiO_2 films with and without pre-nitridation. Ti plates with and without a pre-nitridation were anodized for 30 min using an electrolyte composed of 1.5 M H_2SO_4, 0.1 M H_3PO_4, and 0.3 M H_2O_2.

due to high repassivation capability of Ti [33]. TiN film does not provide a good barrier against further anodization due to its lack of repassivation capability. In addition, TiN films may increase the reactivity with oxygen [34].

From consideration of result in Figs. 5 and 6, it is considered that a pre-nitridation treatment induces the high reactivity in anodization when using electrolyte composed of 1.5 M H_2SO_4, 0.3 M H_3PO_4, and 0.3 M H_2O_2. When using the electrolyte composed of 1.5 M H_2SO_4, 0.1 M H_3PO_4, and 0.3 M H_2O_2, the degree of formation in anatase TiO_2 films and final voltage during anodization are almost same with and without pre-nitridation. However, the anodized specimen with pre-nitridation has higher photocatalytic activity than that without pre-nitridation, due to existence of low valence oxide which retarded photocatalytic activity, as shown in Fig. 7.

Fig. 8 shows the time-course of photocatalytic decomposition of acetaldehyde by anodized TiO_2 films fabricated with various anodization times after a pre-nitridation.

An anodization times were varied from 5 to 60 min. A Ti plate with a pre-nitridation was anodized using an electrolyte composed of 1.5 M H_2SO_4, 0.1 M H_3PO_4, and 0.3 M H_2O_2. A temperature of electrolyte and a current density was set at 20 °C and 4.0 A/dm^2, respectively. The photocatalytic activity initially increased with anodization by 30 min, while it did not increase anymore afterwards. Oh et al. [35] reported that the diameters of the pores are smaller and distributions are more dispersed at an early stage of anodization. Fig. 9 shows the formation of anatase TiO_2 in the anodized TiO_2 films with various anodization times after a pre-nitridation from an evaluation of the integrated anatase TiO_2 XRD intensity. It is clearly seen that the formation of anatase TiO_2 films increased with increasing anodization times. The photocatalytic activity of anodized TiO_2 films was dependent on anodization times. Fig. 10 shows the surface area of the anodized TiO_2 films fabricated with various anodization times after a pre-nitridation
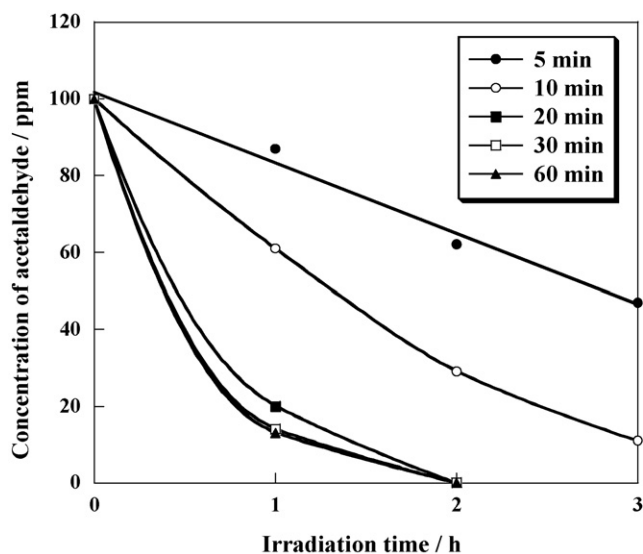
Fig. 8. Time-course of photocatalytic decomposition of acetaldehyde by anodized TiO_2 films fabricated with various anodization times after a pre-nitridation. An anodization times were varied from 5 to 60 min.
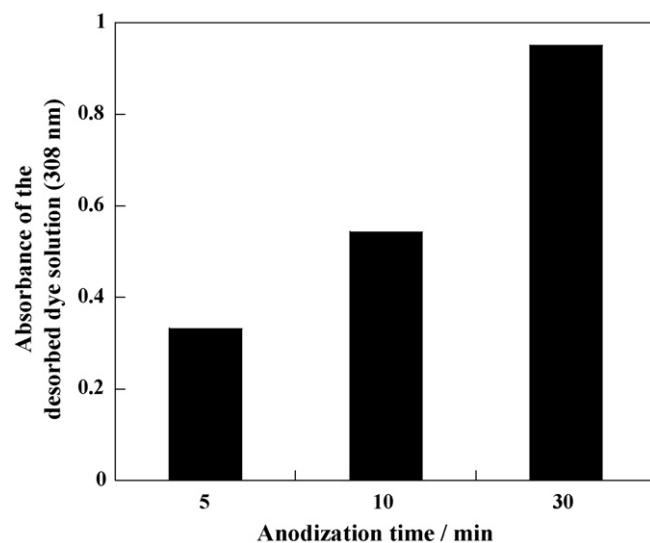

Fig. 10. Surface areas of the anodized TiO_2 films fabricated with various anodization times after a pre-nitridation from evaluation of the concentration of the desorbed dye solution. An anodization times were varied from 5 to 60 min.
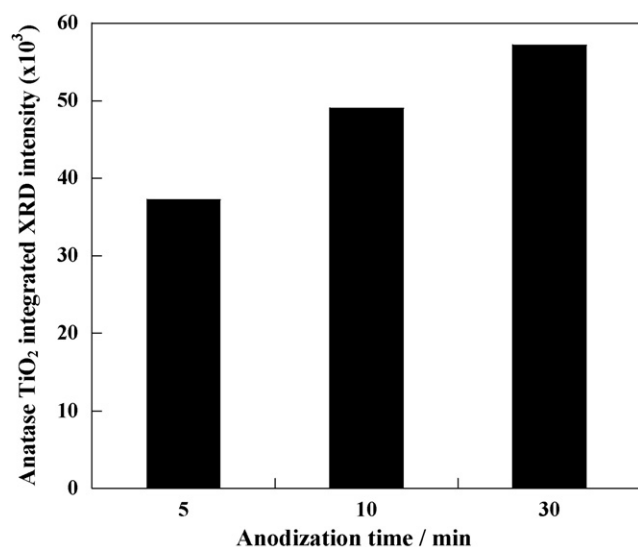

Fig. 9. Formation of anatase TiO_2 in the anodized TiO_2 films with various anodization times after a pre-nitridation from an evaluation of the integrated anatase TiO_2 XRD intensity. An anodization times were varied from 5 to 60 min.

Fig. 11. Time-course of photocatalytic decomposition of acetaldehyde by anodized TiO_2 films fabricated at various current densities after pre-nitridation. A current density was varied from 1.0 to 4.0 A/dm^2.

from evaluation of the concentration of the desorbed dye solution. The surface area of TiO_2 films also increased with increasing anodization times. The photocatalytic activity was also thought to be dependent on the total surface area of photocatalytic TiO_2. It is considered that the surface area of TiO_2 increases with increasing anodization time at the initial stage of less than 30 min, but that of TiO_2 is still constant with anodization time more than 30 min.

Fig. 11 shows the time-course of photocatalytic decomposition of acetaldehyde by anodized TiO_2 films fabricated at various current densities after pre-nitridation. The formation of anatase TiO_2 in anodized specimens was dependent on the current densities. A current density was varied from 1.0 to
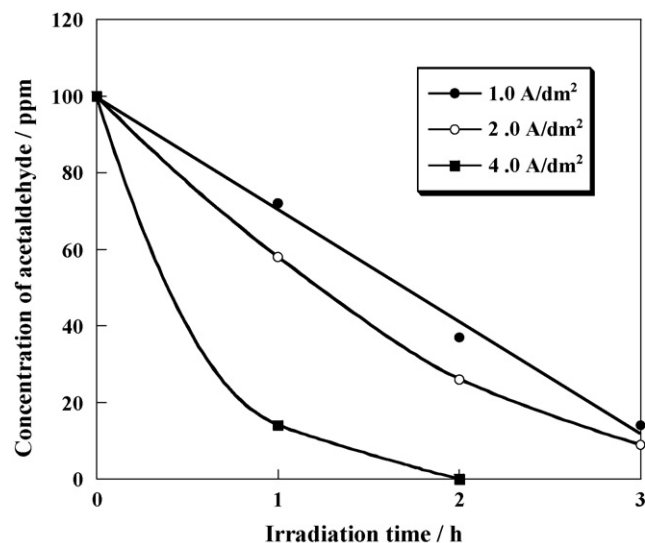
4.0 A/dm^2. A Ti plate with a pre-nitridation was anodized using an electrolyte composed of 1.5 M H_2SO_4, 0.1 M H_3PO_4, and 0.3 M H_2O_2. A temperature of electrolyte and an anodization time was set at 20 °C and 30 min, respectively. It is clearly seen that the photocatalytic activity of the anodized TiO_2 films increased with increasing current density. Figs. 12 and 13 show the formation of anatase TiO_2 films from monitoring the integrated XRD intensity and the surface area of anodized TiO_2 films from monitoring the concentration of the desorbed dye solution, respectively. The current density during anodization was dependent on not only formation of anatase TiO_2 films but also surface area of anodized TiO_2 films. Diamanti and Pedeferri [36] reported that the oxidation rate increased with increasing current density when an anodization was performed in a H_2SO_4 aqueous solution. It is considered that the
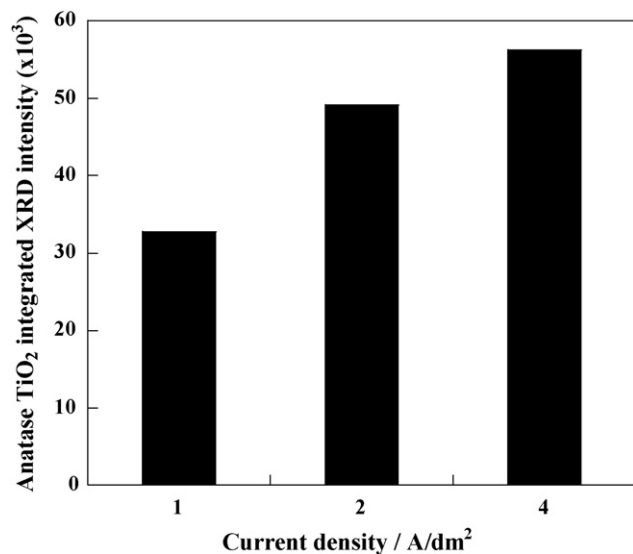
Fig. 12. Formation of anatase TiO_2 in the anodized TiO_2 films fabricated with various current densities after a pre-nitridation from an evaluation of the integrated anatase TiO_2 XRD intensity. A current density was varied from 1.0 to 4.0 A/dm^2.

Fig. 14. Time-course of photocatalytic decomposition of acetaldehyde by anodized TiO_2 films fabricated with various electrolyte temperatures after a pre-nitridation. A temperature of electrolyte was varied with 10 and 20 °C, respectively.

at 1.0 A/dm^2, respectively. It is clearly seen that the photocatalytic activity of the anodized TiO_2 films improved with increasing temperature of electrolyte. It is well-known that the etching ability against a Ti metal is proportional to H_2SO_4 concentration. It is considered that a higher temperature of electrolyte induces a higher reactivity against a Ti metal to improve the photocatalytic activity of the obtained anodized TiO_2 film.

Fig. 15 shows the effect of concentrations of H_3PO_4 on the photocatalytic activity of anodized TiO_2 films for a photodecomposition of acetaldehyde. The electrolyte was composed of 1.5 M H_2SO_4 and 0.3 M H_2O_2 with varying H_3PO_4 concentrations in the range from 0 to 0.5 M. A Ti plate with
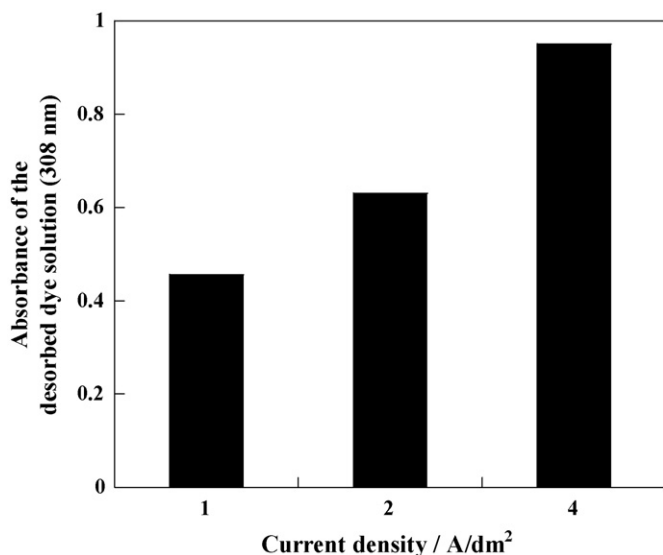

Fig. 13. Surface areas of the anodized TiO_2 films fabricated with various current densities after a pre-nitridation from evaluation of the concentration of the desorbed dye solution. A current density was varied from 1.0 to 4.0 A/dm^2.

anodization with a high current density induces higher oxidation rate to obtain not only larger formation of anatase TiO_2 but also higher surface area of TiO_2. Therefore, a higher current density during anodization can induce the higher photocatalytic activity.

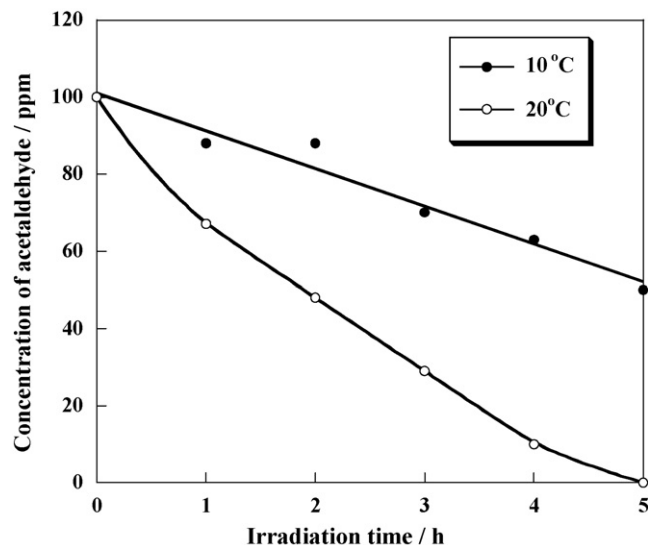Fig. 14 shows time-course of photocatalytic decomposition of acetaldehyde by anodized TiO_2 films fabricated with various electrolyte temperatures after a pre-nitridation. A temperature of electrolyte was varied with 10 and 20 °C, respectively. A Ti plate with a pre-nitridation was anodized using an electrolyte composed of 1.5 M H_2SO_4, 0.1 M H_3PO_4, and 0.3 M H_2O_2. An anodization time and a current density were set for 30 min, and
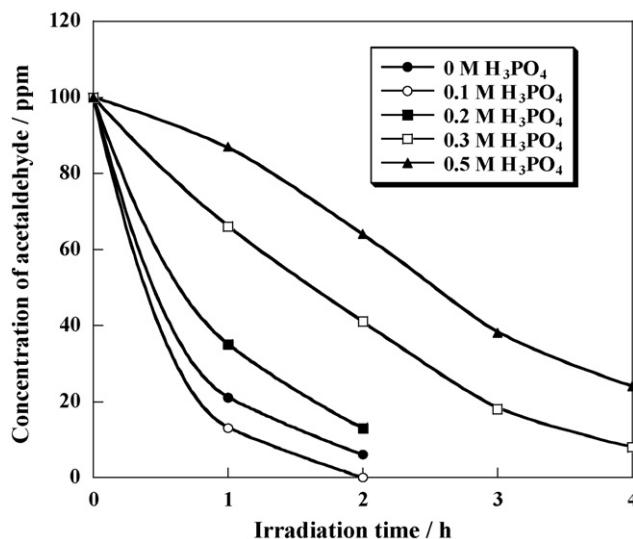

Fig. 15. Effect of concentrations of H_3PO_4 on the photocatalytic activity of anodized TiO_2 films for a photodecomposition of acetaldehyde. The electrolytes were composed of 1.5 M H_2SO_4 and 0.3 M H_2O_2 with varying H_3PO_4 concentrations in the range from 0 to 0.5 M.

a pre-nitridation was anodized at 20 °C for 30 min. A current density was controlled at 4.0 A/dm^2. It is clearly seen that the formation of high performance photocatalytic TiO$_2$ films is promoted by anodization using an electrolyte containing 0.1 M of H$_3$PO$_4$. An anodization of Ti metal in an acidic electrolyte exist a competition between an oxidation reaction to form TiO$_2$ films and a dissolution reaction to release Ti ions from TiO$_2$-electrolyte interface into an electrolyte [37]. Metallic Ti has an excellent corrosion resistance due to an existence of protectively passive TiO$_2$ film on a surface of Ti metal, but it does not resist in a H$_2$SO$_4$ aqueous solution. The existence of H$_2$SO$_4$ in an electrolyte can give a high reactivity against metallic Ti to release Ti ions into an electrolyte. The high reactivity against metallic Ti in anodization process induces the low photocatalytic rutile TiO$_2$ phase through the formation of the high photocatalytic anatase TiO$_2$ phase. On the other hand, it is well-known that H$_3$PO$_4$ is utilized as an electrolyte in a conventional anodization, leading to an obtained amorphous TiO$_2$ layers. Kern and Zinger [38] reported that H$_3$PO$_4$ acted as an inhibitor against the anodization process because the anodization current was lower in the mixture of H$_2$SO$_4$ and H$_3$PO$_4$ than in the electrolyte containing only H$_2$SO$_4$. It is considered that H$_2$SO$_4$ promotes to form the crystalline TiO$_2$ films but H$_3$PO$_4$ inhibits to form the crystalline TiO$_2$ films. For fabricating high performance photocatalytic TiO$_2$ film, a best balance between H$_2$SO$_4$ and H$_3$PO$_4$ concentration is necessary. It is considered that the addition of 0.1 M of H$_3$PO$_4$ as an inhibitor into 1.5 M H$_2$SO$_4$ as an promoter shows the best balance to form high photocatalytic TiO$_2$ film.

Fig. 16 shows that the top view of SEM images of the anodized TiO$_2$ films by anodization in electrolyte of 1.5 M H$_3$PO$_4$ and 0.3 M H$_2$O$_2$ with varying H$_3$PO$_4$ concentrations into 0.1, 0.3, and 0.5 M, respectively. The anodized TiO$_2$ films have porous structures resulting from an electric discharge spark due to the film breakdown [38,39]. It is clearly seen that concentrations of H$_3$PO$_4$ affected on the morphologies of anodized TiO$_2$ films. Fig. 17 shows the surface areas of the anodized specimens from monitoring the desorbed dye solution. From the results in Figs. 16 and 17, the surface areas of anodized films decreased with increasing concentration of H$_3$PO$_4$. It is also clearly seen that H$_3$PO$_4$ acts as an inhibitor against the anodization process. From the results of photo-
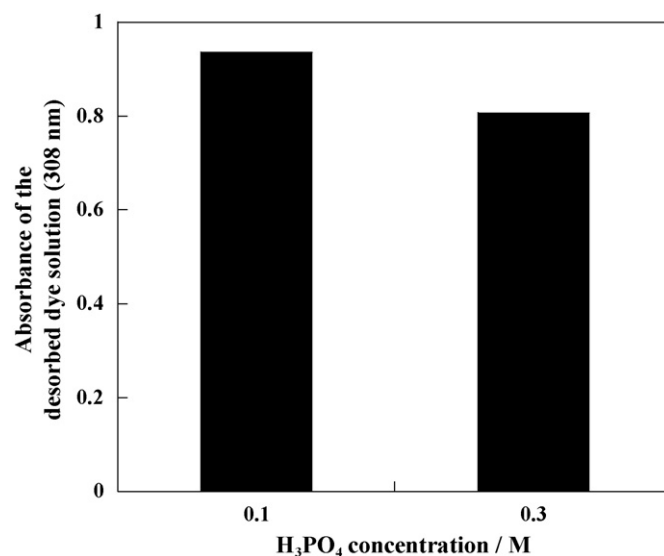

Fig. 17. Surface areas of the anodized TiO$_2$ films fabricated by anodization using various electrolytes after a pre-nitridation from evaluation of the concentration of the desorbed dye. The electrolytes were composed of 1.5 M H$_3$PO$_4$ and 0.3 M H$_2$O$_2$ with varying H$_3$PO$_4$ concentrations into 0.1 and 0.3 M, respectively.

catalytic activity of the anodized TiO$_2$ films for photodecomposition of acetaldehyde, the anodization parameters such as anodization times, current densities, temperature of electrolyte, and composition of electrolyte strongly affect on the photocatalytic activity of the anodized TiO$_2$ films.

Fig. 18 shows the comparison of photocatalytic activities between the anodized TiO$_2$ film and the conventional photocatalyst fabricated by spreading the commercially available coating agent on a Ti metal for a photodecomposition of acetaldehyde. The commercially available coating agent (ST-K211, ST-K101) was obtained from Ishihara Sangyo Kaisha. The Ti plate was polished using the emery paper (#240) and then sonicated in acetone prior to coating process. Afterwards, the Ti plate was coated with ST-K211 at several times after pre-coating ST-K101. The anodized TiO$_2$ film was fabricated by an anodization in an electrolyte composed of 1.5 M H$_2$SO$_4$, 0.1 M H$_3$PO$_4$, and 0.3 M H$_2$O$_2$ subsequent to a pre-nitridation treatment. A Ti plate with a pre-nitridation was anodized at 20 °C for 30 min. A current density was controlled at

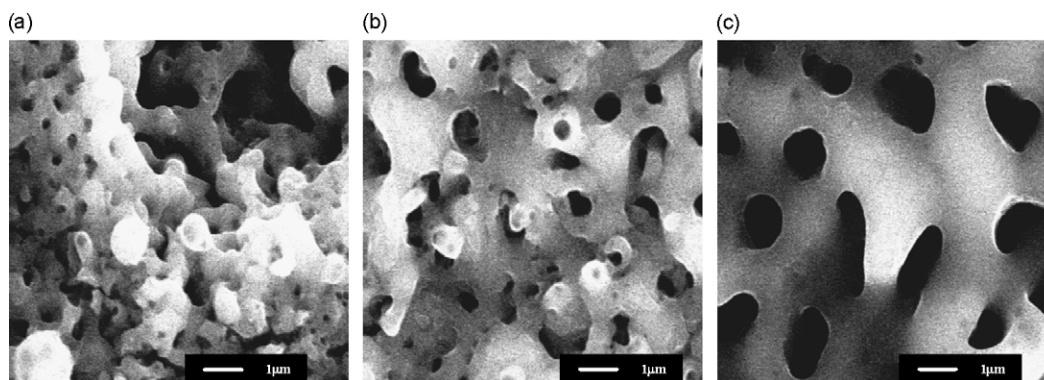
Fig. 16. Top view of SEM images of the anodized TiO$_2$ films by anodization in electrolytes of 1.5 M H$_3$PO$_4$ and 0.3 M H$_2$O$_2$ with varying H$_3$PO$_4$ concentrations into 0.1 M, 0.3 M, and 0.5 M, respectively. A concentration of H$_3$PO$_4$ was (a) 0.1 M, (b) 0.3 M, and (c) 0.5 M.
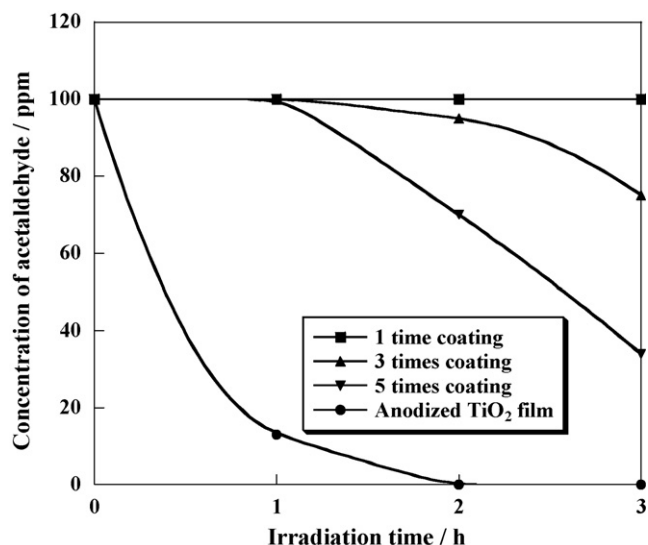
Fig. 18. Comparison of photocatalytic activities between the anodized TiO$_2$ film and the conventional photocatalyst fabricated by spreading the commercially available coating agent on a Ti metal for a photodecomposition of acetaldehyde.

at 4.0 A/dm^2. It is clearly seen that the anodized TiO$_2$ films with a pre-nitridation treatment had a significant high photocatalytic activity, compared with the conventional TiO$_2$ photocatalyst using binder chemicals. In case of the conventional photocatalyst, TiO$_2$ particles slightly scatter at the surface of a specimen, since most particles are buried in binder chemicals, leading to obtaining a low photocatalytic activity. However, the anodized TiO$_2$ films were formed by direct oxidation of TiN film on Ti substrate. The poor photocatalytic activity in the conventional photocatalyst can be explained from small amount of TiO$_2$ photocatalyst on surface of specimens.

Fig. 19 shows the photocatalytic degradation of tetrachloroethylene (PCE) by using the anodized TiO$_2$ films. A Ti plate with a pre-nitridation was anodized for 30 min using an
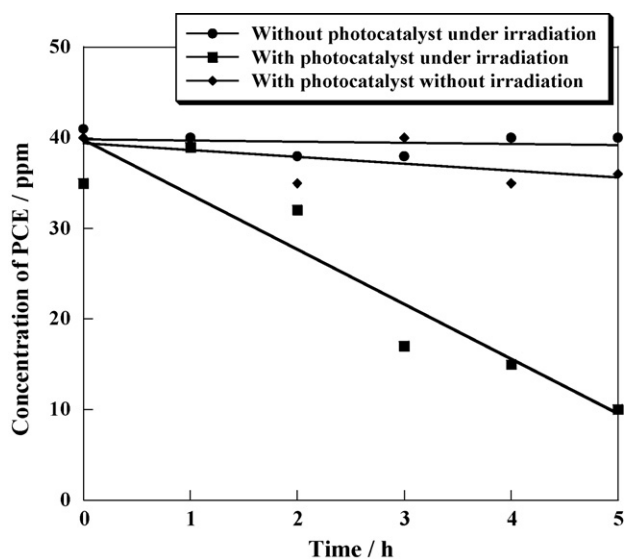
electrolyte composed of 1.5 M H$_2$SO$_4$, 0.1 M H$_3$PO$_4$, and 0.3 M H$_2$O$_2$. A temperature of electrolyte and a current density was set at 20 °C and 4.0 A/dm^2, respectively. It is clearly seen that the degradation of PCE does not occur with photocatalyst without irradiation and with only irradiation. PCE can be degraded by using the anodized TiO$_2$ film as photocatalyst under irradiation. Therefore, the anodized films can also photodegrade a tetrachloroethylene.

4. Conclusions

Metallic Ti with a pre-nitridation treatment was galvanostatically anodized in an electrolyte composed of H$_2$SO$_4$, H$_3$PO$_4$, and H$_2$O$_2$. The photocatalytic activity of anodized TiO$_2$ film for a photodecomposition of acetaldehyde was dependent not only a pre-nitridation but also anodization conditions such as anodization time, current density, electrolyte's temperature, and electrolyte composition. The anodized TiO$_2$ film had a significant high photocatalytic activity than the conventional TiO$_2$ photocatalyst fabricated by using binder chemicals. The anodized TiO$_2$ film with a pre-nitridation also showed the photocatalytic activity to decompose tetrachloroethylene, which is a one of the notorious environmental contaminants. The high performance photocatalytic anodized TiO$_2$ film is a possible candidate for applications of environmental purifications.

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Fig. 19. Photocatalytic degradation of tetrachloroethylene (PCE) by using the anodized TiO$_2$ films.

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